Powder Metallurgy and Metal Ceramics, Vol. 33, Nos. 9-10, 1994

METHODS OF INVESTIGATION OF PROPERTIES OF POWDER MATERIALS

INTERACTIONS IN THE $Al_2O_3-ZrO_2-Y_2O_3$ SYSTEM

S. N. Lakiza, L. M. Lopato,
and A. V. Shevchenko

UDC 546-31:621:641:831

The phase diagram of the $Al_2O_3-ZrO_2$ system was replotted over a broad range of concentrations (0-100 mole %) and temperatures (1150-2800°C). The polymorphic transformation of zirconium $F \rightleftarrows T$ occurs via the metatectic reaction $F \rightleftarrows T + L$ at 2260°C. Phase triangulation was employed to plot the diagrams of the partially quasibinary sections in the $Al_2O_3-ZrO_2-Y_2O_3$ system. Since there is a wide solubility range based on ZrO_2 in the binary $ZrO_2-Y_2O_3$ system, the triangulation conodes are displaced in the F-solid solution corners. The two-phase regions Y_3A_5-F are quite broad. The reactions in all three are of the eutectic type. The ternary solid solution fields in the $Al_2O_3-ZrO_2-Y_2O_3$ system had no observable width.

The $Al_2O_3-ZrO_2-Y_2O_3$ system is one of the most basic to the materials science of high-performance ceramics. Ceramics with high strength (up to 2400 MPa) and impact toughness (up to 10 $MPa \cdot m^{1/2}$) are obtained in this system, in which, depending upon the composition, various mechanisms for increasing the strength and toughness are active: transformation (ZrO_2-based material), dispersion hardening (Al_2O_3-based material), fiber reinforcement (directionally solidified eutectics $Al_2O_3-ZrO_2(Y_2O_3)$, $Al_2O_3-Y_3Al_5O_{12}$), etc. Materials based on Y_2O_3 are used for the fabrication of high-temperature windows, stable in aggressive media and transparent in the visible and near (about 2 μm) IF regions of the spectrum. A knowledge of the phase diagram is essential to the successful preparation of materials based on the above system.

The bounding two-component systems have been thoroughly investigated and their phase diagrams constructed [1-14]. The liquidus in the $Al_2O_3-ZrO_2$ system is of the eutectic type. New phases do not appear. According to data in the literature, the components are mutually insoluble in the solid state. However, the polymorphic transformations in ZrO_2 are not reflected in the phase diagrams known from the literature. The $Al_2O_3-Y_2O_3$ system is characterized by the presence of three congruently melting compounds: $Y_3Al_5O_{12}(Y_3A_5)$, $YAlO_3(YA)$, and $Y_4Al_2O_9(Y_2A)$ existing over a wide temperature interval and without a range of homogeneity. Solid solutions based on the initial components do not exist. The $ZrO_2-Y_2O_3$ system above 1400°C is one of the number which exhibit limited solubility of the components in the solid state. Solid solutions based on the monoclinic (M), tetragonal (T), and cubic (fluorite type) modifications of ZrO_2 (F), and also the hexagonal (H) and cubic (C-type oxides of the REM) modifications of Y_2O_3 (C) are formed.

The phase diagram of the $Al_2O_3-ZrO_2-Y_2O_3$ system has not been sufficiently investigated. Only the isothermal sections at 1250, 1450, 1600, 1650, and 1800°C have been studied [15-18]. There is no data on the shape of the liquidus surface. Based on the phase diagrams of the bounding two-component systems it may be assumed that three quasibinary sections exist: $ZrO_2-Y_3A_5$, ZrO_2-YA, and ZrO_2-Y_2A.

The objective of the present work was to improve the accuracy of the phase diagrams of the binary systems $ZrO_2-Al_2O_3$ and $Al_2O_3-Y_2O_3$ in the regions with high concentrations of ZrO_2 and Y_2O_3, triangulate the phase diagram of the ternary system $Al_2O_3-ZrO_2-Y_2O_3$, and construct diagrams for the quasibinary sections

Analysis of the 1250, 1650, and 1800°C isothermal sections [16-18] of the system under investigation indicates that the yttrium aluminides Y_3A_5, YA, and Y_2A are found in equilibrium not with pure ZrO_2, but with a solid solution F containing various amounts of Y_2O_3. Corresponding two-phase regions of various extent appear in the concentration triangle.

Institute of Materials Science Problems, Ukrainian Academy of Sciences, Kiev. Translated from Poroshkovaya Metallurgiya, Nos. 9/10, pp. 46-51, September-October, 1994. Original article submitted June 30, 1993.

 1068-1302/94/0910-0486$12.50

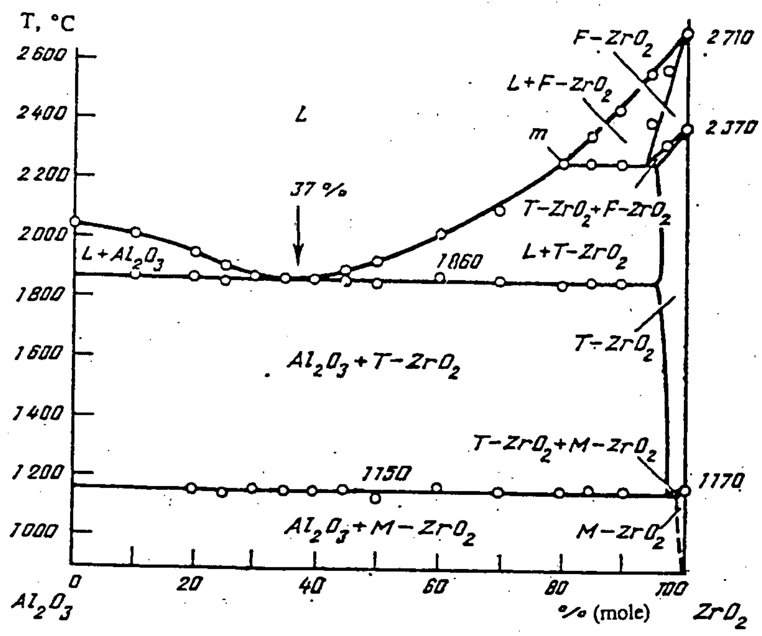

Fig. 1. Phase diagram of the $Al_2O_3-ZrO_2$ system according to the data in [1-4] and the results of the present investigation.

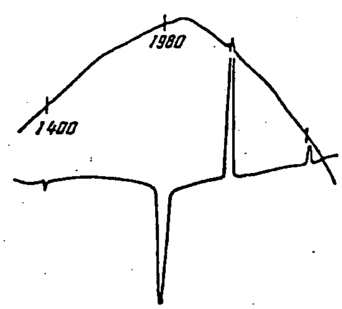

Fig. 2

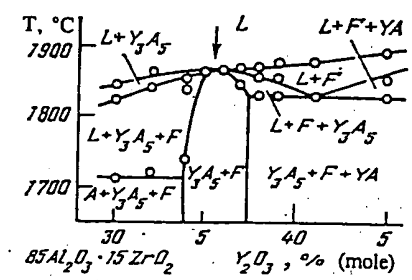

Fig. 3

Fig. 2. Heating and cooling curves for the compound $Y_4Al_2O_9$ (Y_2A).

Fig. 3. Concentration dependence of the solidus temperature of the two-phase alloys Y_3A_5-F along the 15 mole% ZrO_2 line in the $Al_2O_3-ZrO_2-Y_2O_3$ system.

The two-phase region in the Y_3A_5-F system is particularly broad. Phase-equilibrium theory [19] states that quasi-binary sections are not possible in a ternary system with broad homogeneity regions based on the primary and intermediate phases, i.e., there are no sections in the planes of which the compositions of the phases coexisting in equilibrium lie at all temperatures. However, certain sections or phase regions in a ternary system may possess the defining features of a quasibinary system. A necessary condition is satisfaction of the Van-Rheins rule, that the lowest figurative point for the liquid composition in such a section must be a crossover point (saddle point) on the liquidus surface of the ternary system, or a maximum on the solidus surface [20].

Since the regions of two-phase equilibrium $YA-F$ and Y_2A-F are narrow (the composition of F varies within the limits 4-5 mole %), it may be assumed that partially quasibinary sections pass through their centers. The two-phase region Y_3A_5-F, as mentioned above, is quite broad (the composition of the solid solution F in equilibrium with Y_3A_5 lies in the range 18.5-37.0 mole % Y_2O_3), and locating the partially quasibinary section in this case requires a more precise definition.

The initial powders – grade ChDA (TU 6-09-426–75) Al_2O_3, Donetsk Chemical Plant grade Ch (TU 6-09-2486–77) ZrO_2, and grade ITO-Lyum Y_2O_3 from the pilot plant of the Ukrainian Academy of Sciences Physical Chemistry Institute (Odessa) – were ground in an agate mortar in ethyl alcohol, and then compacted into tablets 5 mm in both diameter

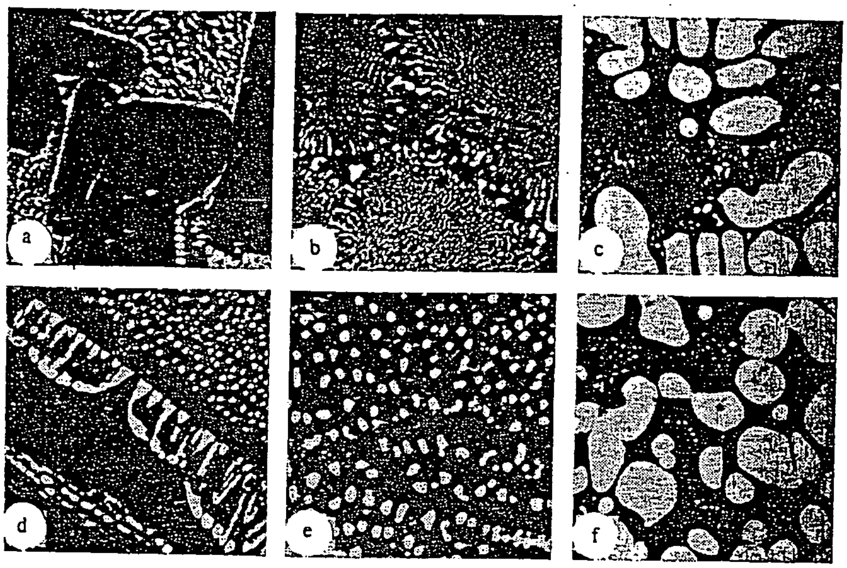

Fig. 4. Electron microphotographs of some alloys in the partially quasibinary sections of the phase diagram of the $Al_2O_3-ZrO_2-Y_2O_3$ system. ZrO_2 concentration (mole%): (a) 13 {Y_3A_5, eutectic Y_3F_5 + F}; (b) 15 {eutectic Y_3A_5 + F}; (c) 35 {F, eutectic Y_3A_5 + F}; (d) 5 {YA, eutectic YA + F}; (e) 11.5 {eutectic YA + F}; (f) 14 {F, eutectic Ya + F}. Magnification: (a) 1200; (b) 2000; (c) 1000; (d) 1500; (e) 2500; (f) 1100.

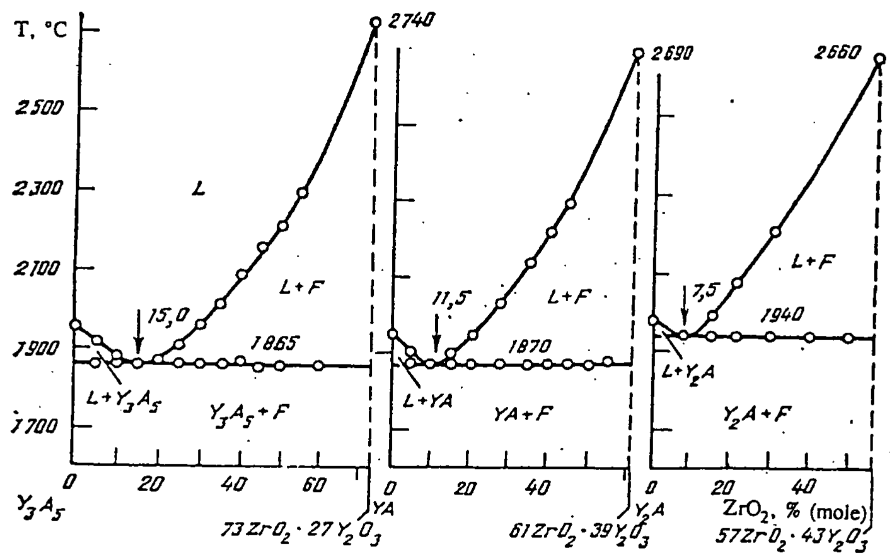

Fig. 5. Partially quasibinary sections in the phase diagram of the $Al_2O_3-ZrO_2-Y_2O_3$ system: (a) $Y_3A_5-73ZrO_2{\cdot}27Y_2O_3$ (F_1); (b) $YA-61ZrO_2{\cdot}39Y_2O_3$ (F_2); (c) $Y_2A-57ZrO_2{\cdot}43Y_2O_3$ (F_3).

and height. The concentration intervals were taken as 5 mole %. In the Y_3A_5-F specimens designated for investigation of the concentration dependence of the solidus temperature these were taken as 1 mole%. Heat treatment up to 2500°C [21] was carried out in a DTA unit in an atmosphere of helium, using a molybdenum crucible. The specimens were studied by the DTA method up to 2500°C [21]. by the method of derivative thermal analysis (PTA) in air up to 3000°C (accuracy ±20°C) using a helio-unit [7], and by the methods of diffractometric (DRON-1,5, CuK_α radiation, Ni filter), petrographic (MIN-8), and microstructural (MIM-7. Kamebaks SKh-50) phase analysis. Polished sections were prepared by grinding on diamond discs and polishing with diamond pastes of various particle sizes.

Firstly, certain elements in the phase diagrams of the bounding two-phase systems were determined with greater precision. Figure 1 shows the phase diagram of the $Al_2O_3-ZrO_2$ system, constructed according to the data of [1-4] and the

results obtained by us. It was found that the temperature of the polymorphic transformation F ⇄ T in zirconium dioxide (2370°C) decreases with increasing Al_2O_3 concentration to 2260°C. This transformation appears on the liquidus in the form of the metatectic point m at 20 mole% Al_2O_3. The coordinates of the eutectic point are 1860°C and 37 mole% ZrO_2. The polymorphic transformation in the solid state T ⇄ M is of the eutectoid type, and its temperature varies from 1170 to 1150°C. The solubility limit in ZrO_2 does not exceed 5 mole% at the metatectic temperature (2260°C), and decreases substantially with decreasing temperature.

In the $Al_2O_3-Y_2O_3$ system, the temperature of the polymorphic transformation of yttrium oxide (2350°C) is unaffected by additions of Al_2O_3, which is in accord with the insolubility of alumina in Y_2O_3 at elevated temperatures, and the appearance of a degenerate metatectic point m on the binary system liquidus at the coordinates 2350°C and 4 mole% Al_2O_3. More precise melting temperatures for the yttrium aluminides are: Y_3A_5 (1950°C), YA (1925°C), Y_2A (1980°C); and for the binary eutectics: $Al_2O_3-Y_3A_5$ (1825°C), Y_3A_5-YA (1900°C), $YA-Y_2A$ (1900°C), $Y_2A-Y_2O_3$ (1930°C). An endothermic effect at 1400°C is observed on the heating curves for Y_2A (Fig. 2). This was explained by N. A. Toropov, et al., [8] as due to a polymorphic transformation which was detected by high-temperature crystal optic studies at 1000°C. Other scholars [22] consider that at this temperature Y_2A decomposes into Y_3A_5 and Al_2O_3. It was established by us, with the aid of high-temperature x-ray diffraction studies, that at temperatures above the DTA effect at 1400°C the specimen possesses the low temperature monoclinic structure of Y_2A. The nature of the observed effect is not clear.

The concentration dependence of the solidus temperature in two-phase Y_3A_5-F alloys along the 15 mole% ZrO_2 isoconcentration line in the $Al_2O_3-ZrO_2-Y_2O_3$ ternary system is shown in Fig. 3. The maximum solidus temperature corresponds to 35.5 mole% Y_2O_3 in the section $Y_3A_5-73ZrO_2{\cdot}27Y_2O_3$ (F_1), i.e., the eutectic horizontal L ⇄ Y_3A_5 + F_1 lies in the plane of this section in the phase diagram of the $Al_2O_3-ZrO_2-Y_2O_3$ system. The indicated section, as mentioned above, is not quasibinary in the strict sense of this term, according to which the conodes for the three-phase equilibrium L ⇄ Y_3F_5 + F_1 lie only in the plane of the given section. When the temperature is decreased the conode for the Y_3A_5 phase in equilibrium with the solid solution F phase containing various amounts of Y_2O_3 moves out of the plane of this section. All of the above relates also to the sections $YA-F_2$ (39 mole% Y_2O_3) and Y_2A-F_3 (43 mole% Y_2O_3).

X-ray diffraction analysis of alloys in the sections $Y_3A_5-F_1$, $YA-F_2$, and Y_2A-F_3 revealed that there are two phases in every specimen: solid solutions F based on cubic ZrO_2 with various concentrations of Y_2O_3 plus Y_3A_5, YA, and Y_2A, respectively. Figure 4 shows the microstructures of a number of alloys related to the investigated sections. The microstructures are two-phased, consisting of primary crystals of Y_3A_5(YA, Y_2A) in hypoeutectic specimens or solid solutions F of various compositions in hypereutectic, and the corresponding binary eutectics Y_3A_5 + F, YA + F, and Y_2A + F. The petrographic data confirmed the results of microstructural analysis.

The partially quasibinary sections $Y_3A_5-F_1$, $YA-F_2$, and Y_2A-F_3 in the phase diagram of the $Al_2O_3-ZrO_2-Y_2O_3$ system from 1600-2800°C are shown in Fig. 5. All of the reactions are of the eutectic type. The primary phases exhibit no solubility range. The eutectic compositions contain 15.0, 11.5, and 7.5 mole% ZrO_2, respectively, in the sections $Y_3A_5-F_1$, $YA-F_2$, and Y_2A-F_3; the melting temperatures are 1865, 1870, and 1940°C. These are, at the same time, saddle points in the $Al_2O_3-ZrO_2-Y_2O_3$ system. There are no phase transformations in the solid state above 1600°C in the investigated sections.

REFERENCES

1. F. Schmid and D. Viechnicki, "Oriented eutectic microstructures in the system $Al_2O_3-ZrO_2$," J. Mater. Sci., **5**, No. 6, 470-473 (1970).
2. G. R. Fischer, L. J. Manfredo, R. N. McNally, et al., "The eutectic liquidus in the $Al_2O_3-ZrO_2$ system," Ibid., **16**, No. 12, 3447-3451 (1981).
3. J. Echigoya, Y. Takabayashi, K. Sasaki, et al., "Solidification microstructure of Y_2O_3-added $Al_2O_3-ZrO_2$ eutectic," Trans. Jap. Inst. Metals, **27**, No. 2, 102-107 (1986).
4. A. V. Shevchenko, L. M. Lopato, G. I. Gerasimyuk, et al., "The $HfO_2-ZrO_2-Al_2O_3$ system," Izv. Akad. Nauk. SSSR, Neorgan. Mater., **26**, No. 4, 839-842 (1990).
5. V. S. Stubican, R. G. Hink, and S. P. Ray, "Phase equilibrium and ordering in the system $ZrO_2-Y_2O_3$," J. Amer. Ceram. Soc. **61**, Nos. 1-2, 17-21 (1978).

6. A. V. Shevchenko, V. D. Tkachenko, L. M. Lopato, et al., "Method for determining phase transformation temperatures with the use of solar heating," Poroshk. Metall., No. 1, 91-95 (1986).
7. A. V. Shevchenko, L. M. Lopato, T. V. Obolonchik, et al., "Liquidus surface in the system $HfO_2-ZrO_2-Y_2O_3$," Izv. Akad. Nauk. SSSR, Neorg. Mater., **23**, No. 3, 452-456 (1987).
8. N. A. Toropov, I. A. Bondar', F. Ya. Galakhov, et al., "Phase equilibria in the yttrium oxide–alumina system," Izv. Akad. Nauk. SSSR, Ser. Khim., No. 7, 1158-1164 (1964).
9. D. Viechnicki and F. Schmid, "Investigation of the eutectic point in the system $Al_2O_3-Y_3Al_5O_{12}$," Mater. Res. Bull., **4**, No. 2, 129-135 (1969).
10. J. L. Caslavski and D. J. Viechnicki, "Melting behavior and metastability of yttrium aluminum garnet (YAG) and $YAlO_3$ determined by optical differential thermal analysis," J. Mater, Sci., **15**, No. 7, 1709-1718 (1980).
11. I. A. Bondar', L. N. Koroleva, and E. T. Bezruk, "Physicochemical properties of yttrium aluminates and gallates," Izv. Akad. Nauk. SSSR, Neorgan. Khim., **20**, No. 2, 257-261 (1984).
12. B. Cockayne, "The uses and enigmas of the $Al_2O_3-Y_2O_3$ system," J. Less Common Metals, **114**, No. 1, 199-206 (1985).
13. G. T. Adylov, G. V. Voronov, É. P. Mansurova, et al., "The $Y_2O_3-Al_2O_3$ system above 1473 K," Zhur. Neorgan. Khim., **33**, No. 7, 1867-1869 (1988).
14. Tail-il Mah and M. D. Petry, "Eutectic composition in the pseudobinary of $Y_4Al_2O_9$ and Y_2O_3," J. Amer. Cer. Soc., **75**, No. 7, 2006-2009 (1992).
15. W. D. Tuohig and T. Y. Tien, "Subsolidus phase equilibria in the system $ZrO_2-Y_2O_3-Al_2O_3$," ibid., **63**, Nos. 9-10, 595-596 (1980).
16. S. G. Popov, S. F. Pashin, M. V. Paromova, et al., "Subsolidus phase equilibria in the system $ZrO_2-Y_2O_3-Al_2O_3$," Izv. Akad. Nauk. SSSR, Neorg. Mater., **26**, No. 1, 113-117 (1990).
17. L. M. Lopato, L. V. Nazarenko, G. I. Gerasimyuk, et al., "Reactions in the system $ZrO_2-Y_2O_3-Al_2O_3$ at 1650°C," Ibid., No. 4, 834-838 (1990).
18. L. M. Lopato, L. V. Nazarenko, G. I. Gerasimyuk, et al., "Isothermal section of the phase diagram of the system $ZrO_2-Y_2O_3-Al_2O_3$ at 1250°C," Ibid., **28**, No. 4, 835-839 (1992).
19. A. M. Zakharov, Phase Diagrams of Binary and Ternary Systems [in Russian], Metallurgiya, Moscow (1990).
20. V. N. Eremenko, T. Ya. Velikanova, L. V. Artyukh, et al., Ternary Systems of Molybdenum with Carbon and the Group IV Transition Metals [in Russian], Nauk. Dumka, Kiev (1985).
21. L. M. Lopato, A. V. Shevchenko, and A. E. Kushchevskii, "Investigation of high-energy oxide systems," Poroshk. Metall., No. 1, 88-92 (1972).
22. I. Warshaw and R. Roy, "Stable and metastable equilibria in the systems $Y_2O_3-Al_2O_3$ and $Gd_2O_3-Fe_2O_3$," J. Amer. Cer. Soc., **42**, No. 9, 434-438 (1959).

THIS PAGE BLANK (USPTO)